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Adsorption of Aniline Derivatives on Platinum Electrode in Aqueous Alkaline Solution

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Synopsis. In the adsorption of aniline derivatives on Pt electrode, a linear relation was observed between the chemical shift of the *m*- and *p*-amino protons and the inhibiting effect on the anodic oxidation of methanol. However, *o*-alkylanilines and chloroanilines showed deviations due to steric hindrance and strong interactions, respectively.

Earlier papers[1,2] pointed out that the adsorption phenomena in the electrode-solution interphase is possibly related to the overvoltage of the electrochemical reaction on the electrode. The influence of the structures of some organic compounds on the adsorption has also been reported[3,4] with reference to corrosion inhibitors. Cox and his co-workers[5] reported on the relationship between the NMR chemical shift of the amino protons of the aromatic inhibitors and the corrosion-inhibiting effect on iron in hydrochloric acid. Furthermore, some works[6-8] have referred to the inductive effects of the anchoring groups in organic compounds in connection with corrosion inhibition. The mechanism[3] of the adsorption of organic compounds containing nitrogen was investigated with reference to the iron in acids and with reference to the platinum in an aqueous alkaline solution.[9] Previous reports suggested a strong inhibition of chloro-substituted alkylamines[10,11] and allyl halides.[12]

The nitrogen atoms of organic amines and pyridine homologues can occupy anchoring positions on the adsorption on the platinum electrode in an aqueous alkaline solution, because of their strong electronegativity. However, the halogen atoms in organic compounds are also electronegative, and they may also be expected to occupy the anchoring positions. The purpose of this work is, then, to clarify the mechanism of the adsorption of the aniline derivatives on the platinum electrode in aqueous alkaline solution. The adsorption of the aniline derivatives on the electrode is estimated by measuring the influence on the peak current of the current-potential curves in the anodic oxidation of methanol.

Experimental

The sodium hydroxide, methanol, and aniline were guaranteed reagents by the Japanese Industrial Standards. The *m*- and *p*-chloroanilines, *o*-, *m*-, and *p*-methylanilines, *p*-ethylaniline, 2,4-dimethylaniline, *N*-methylaniline, and *N*,*N*-dimethylaniline were also guaranteed reagents, while the *o*-ethylaniline was an extra pure reagent made by the Wako Pure Chemical Ind. Co., Ltd. The purity of these reagents was detected by ascertaining one peak on the gas chromatograms. The carbon tetrachloride used in NMR measurements was a spectrometric-grade reagent made by the Nakarai Chemicals Co., Ltd.

The electrolytic cell and the instrument used for the potential sweep voltammetry were identical with those previously described.[13] The test electrode was a platinum plate with dimensions of $1\times1\times0.05$ cm^3; it was pretreated as in the previous work.[13] The electrolyte solution was deoxygenized by bubbling argon gas for 10 min before electrolysis.

The adsorption of aniline derivatives on the platinum electrode was estimated by measuring the influence of the peak current of methanol added to the electrolyte solution on the potential-current curves by single-sweep voltammetry.[13,14] The inhibition of the anodic oxidation of methanol as a measure of the adsorption was calculated by using Eq. (1):

Degree of the inhibiting effect

$$= [(i_0-i)/i_0] \times 100\ (\%) \tag{1}$$

where i_0 is the current on the electrode in the solution without the aniline derivatives and where i is that in the solution with the aniline derivatives. The NMR spectra of the aniline derivatives in carbon tetrachloride were measured on a JNM 3H-60 spectrometer (Nippon Denshi Co., Ltd.), with tetramethylsilane as the internal standard.

Results and Discussion

In the single-sweep voltammetry, the potential of the test electrode was initially maintained at -400 mV (*vs.* Hg/HgO/1 M KOH) for 15 min and was then swept anodically, at the rate of 100 mV/s, in aqueous solutions of potassium hydroxide containing aniline and methanol. The anodic current peaks were observed at about -140 mV on the current-potential curve for the aqueous solution of 1 M potassium hydroxide containing 0.5 mol/l methanol. These peaks were caused by the adsorption and electro-oxidation of methanol. This process was irreversible, and a linear relation was observed between the peak potentials and the logarithms of the potential sweep rate in the range from 0.001 to 0.4 V/s.

We also measured the influence of the concentration of aniline in 1 M aqueous potassium hydroxide containing 0.5 mol/l methanol on the degree of the inhibiting effect of the anodic oxidation of methanol, as is shown in Table 1. From these results, the proper concentration of the aniline derivatives for the test was determined to be 5×10^{-4} mol/l. The peak potential for the anodic oxidation of methanol was shifted in the anodic direction according to the addition of aniline; it was -85 mV (*vs.* Hg/HgO/1 M KOH) in an aqueous solution containing 1 M potassium hydroxide, 0.5 mol/l methanol, and 5×10^{-4} mol/l aniline. With regard to the accuracy of the inhibiting effect (percent), the standard deviation for five measurements was 1.3 percent in the solution cited above. However,

Table 1. Inhibiting effect of aniline on the anodic oxidation of methanol in aqueous potassium hydroxide. (concentration: 1 M KOH, 0.5 M CH_3OH), 25°C.

Concentration of aniline M	Inhibiting effect %
10^{-2}	95.5
5×10^{-3}	89.3
10^{-3}	85.0
5×10^{-4}	72.4
10^{-4}	64.0
5×10^{-5}	42.0
10^{-5}	33.1
5×10^{-6}	16.7
10^{-6}	8.8

these peak potentials were almost constant with the variation in the concentration of methanol in the range from 0.01 to 1 mol/l.

The mechanism of the adsorption of aniline derivatives on the platinum electrode is presumed to be related to the variation in the electron densities, and it probably has some relation with the chemical shift of the NMR spectra of these derivatives. For example, in these experiments, the chemical shifts of the amino protons of aniline and *p*-chloroaniline were observed at 6.69 and 6.61 ppm respectively. In this case, it was found from the spectra that the chemical shift of the amino protons was displayed at a field 0.08 ppm lower than that in aniline as a result of the introduction of the chloro-substituent. Similarly, the chemical shift of the amino proton of *p*-chloroaniline was in a lower magnetic field because of the strong electrophilicity of the chlorine atom. Figure 1 shows the relations between these chemical shifts of the amino protons of the aniline derivatives and the inhibiting effect on the anodic current of methanol in aqueous potassium hydroxide resulting from the adsorption of the derivatives on the electrode.

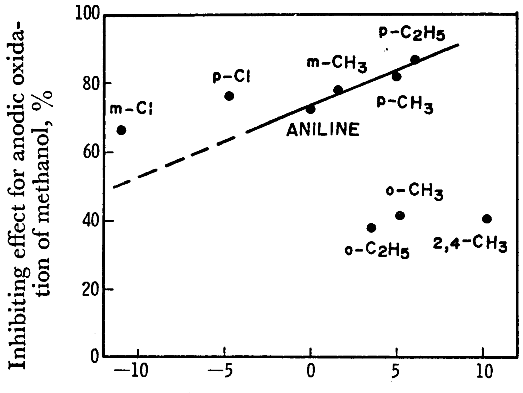

Fig. 1. Chemical shift of the amino protons of aniline derivatives plotted against the inhibition of the anodic oxidation of methanol. 25 °C.

As has been reported in previous reports,[5–9] the adsorption of the organic compounds containing nitrogen is related to the variation in the electron densities around the nitrogen atoms caused by the effects of resonance and hyperconjugation and by the inductive effect. In Fig. 1, a linear relation may be observed between the chemical shifts of the amino protons and the inhibiting effect of the anodic oxidation of methanol with regard to the *p*- and *m*-alkylanilines. However, the steric hindrance of the *o*-alkylanilines to the anchoring nitrogen atom gave large deviations from the linear relation shown in Fig. 1. In the case of the additions of 5×10^{-4} mol/l *N*-methylaniline and *N,N*-dimethylaniline, the inhibiting effects were 23.0 and 9.3% respectively. These low effects probably depend on the strong steric hindrance to nitrogen atoms in the molecules.

Furthermore, the deviations of the chloroanilines were observed in the direction opposite from that shown in Fig. 1; this phenomenon suggests some direct combination of the chlorine atom with the electrode. These results correspond with the previous experimental results [10–12] that the inhibiting effect of chlorinated alkylamines and allyl halides on the corrosion of iron is stronger than that of the corresponding alkylamines and allyl compounds.

The results suggest that there is a linear relation between the chemical shifts of the amino protons of *m*- and *p*-alkylanilines and the inhibiting effect of the aniline derivatives on the anodic oxidation of methanol on a platinum electrode in an aqueous alkaline solution, but *o*-alkylanilines and chloroanilines showed deviations from this relation. The anchoring site of these derivatives should be the nitrogen atom, but some steric hindrance was observed with the *o*-alkylanilines and some strong interactions were observed on *m*- and *p*-chloroanilines respectively.

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References

1) N. Isgarishev and S. Berkmann, *Z. Elektrochem.*, **28**, 40 (1923).
2) S. Glasstone, *Trans. Faraday Soc.*, **21**, 36 (1925).
3) N. Hackerman and A. C. Markides, *Ind. Eng. Chem.*, **46**, 523 (1954).
4) N. Hackerman, *Corrosion*, **18**, 332t (1962).
5) P. F. Cox, R. L. Every, and O. L. Riggs, Jr., *ibid.*, **20**, 299t (1965).
6) F. M. Donahue and K. Nobe, *J. Electrochem. Soc.*, **112**, 886 (1965).
7) H. Tamura, Y. Matsuda, and M. Iijima, *Kogyo Kagaku Zasshi*, **72**, 1077 (1969).
8) J. Vosta and J. Eliasek, *Corros. Sci.*, **11**, 223 (1971).
9) Y. Matsuda and H. Tamura, *Electrochimica Acta*, **14**, 427 (1969).
10) Y. Matsuda, Y. Kinuhata, M. Okahara, S. Komori, and H. Tamura, *Corros. Sci.*, **10**, 179 (1970).
11) H. Tamura, Y. Matsuda, Y. Kinuhata, M. Okahara, and S. Komori, *Kogyo Kagaku Zasshi*, **73**, 438 (1970).
12) S. Nakagawa and G. Hashizume, *Denki Kagaku*, **38**, 831 (1970).
13) H. Tamura, Y. Matsuda, and C. Iwakura, *Kogyo Kagaku Zasshi*, **71**, 1141 (1968).
14) K. Sasaki, I. Izumi, K. Ohashi, T. Uemura, and S. Nagaura, *Nippon Kagaku Zasshi*, **87**, 918 (1966).